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There has been a tremendous recent interest in the development of second-order nonlinear optical (NLO) polymeric materials for photonic applications. However, a major drawback of second-order NLO polymers that prevents them from being used in device applications is the instability of their electric field induced dipolar alignment. The randomization of the dipole orientation leads to the decay of second-order optical nonlinearities. Numerous efforts have been made to increase the stability of the second-order NLO properties of polymers. The search for new approaches to develop NLO polymers with optimal properties has been an active research area since the past decade. A novel approach, combining the hybrid properties of high glass transition temperatures, extensively crosslinked networks, and permanent entanglements, based on interpenetrating polymer networks (IPN) is introduced to develop stable second-order NLO materials. Two types of IPN systems are prepared and their properties are investigated. The designing criteria and the rationale for the selection of polymers are discussed. the IPN samples show excellent temporal stability at elevated temperatures. Long term stability of the optical nonlinearity at 100°C has been observed in these materials. Temporal stability of the NLO properties of these IPNs is synergistically enhanced. Relaxation behavior of the optical nonlinearity of an IPN system has been studied and compared with that of a typical guest/host system. The improved temporal stability of the second-order NLO properties of this IPN system is a result of the combination of the second-order NLO properties of this IPN system is a result of the combination of the high rigidity of the polymer backbones, crosslinked matrices, and permanent entanglements of the polymer networks. A slight modification of the chemical structure resulted in an improvement of the optical quality of the sample.

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Interpenetrating polymer network, second-order nonlinear optic polymer, poling, sol-gel.

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# Design and Synthesis of Interpenetrating Polymer Networks for Second-Order Nonlinear Optics

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# ABSTRACT

There has been a tremendous recent interest in the development of second-order nonlinear optical (NLO) polymeric materials for photonic applications. However, a major drawback of second-order NLO polymers that prevents them from being used in device applications is the instability of their electric field induced dipolar alignment. The randomization of the dipole orientation leads to the decay of second-order optical nonlinearities. Numerous efforts have been made to increase the stability of the second-order NLO properties of polymers. The search for new approaches to develop NLO polymers with optimal properties has been an active research area since the past decade.

A novel approach, combining the hybrid properties of high glass transition temperatures, extensively crosslinked networks, and permanent entanglements, based on interpenetrating polymer networks (IPN) is introduced to develop stable second-order NLO materials. Two types of IPN systems are prepared and their properties are investigated. The designing criteria and the rationale for the selection of polymers are discussed. The IPN samples show excellent temporal stability at elevated temperatures. Long term stability of the optical nonlinearity at 100 °C has been observed in these materials. Temporal stability of the NLO properties of these IPNs is synergistically enhanced. Relaxation behavior of the optical nonlinearity of an IPN system has been studied and compared with that of a typical guest/host system. The improved temporal stability of the second-order NLO properties of this IPN system is a result of the combination of the high rigidity of the polymer backbones, crosslinked matrices, and permanent entanglements of the polymer networks. A slight modification of the chemical structure resulted in an improvement of the optical quality of the sample.

# I. Introduction

Nonlinear optical (NLO) materials have been of active research interest since the past decade owing to their potential applications in integrated optical devices, such as waveguide electro-optic modulators, switches and optical frequency doubling devices. The development of polymeric materials for second-order NLO applications is considered very promising due to their large optical nonlinearities, low dielectric constants and ease of waveguide processability. A considerable volume of work has been reported in the area of the second-order NLO polymers.[1]

In order to impart second-order NLO properties, polymeric materials are incorporated with NLO chromophores. The NLO chromophores usually possess electron donor- and acceptor groups attached to an aromatic ring system in order to increase charge transfer through $\pi$-electron delocalization.[2] These chromophores are characterized by intramolecular charge transfer giving rise to large ground and excited state dipole moments and second-order molecular hyperpolarizability. In the bulk state, these NLO chromophores have to be aligned in a noncentrosymmetric fashion so that the individual molecular susceptibilities do not cancel out and the system exhibits second-order nonlinearity. The alignment of dipoles in polymer matrices is often achieved by a technique called 'poling'.

The poling process is usually carried out by applying an external electric field across the polymer film at temperatures near the glass transition temperature ($T_g$) of the polymer matrix.[3,4] The active moieties are subsequently 'frozen' in the poled phase by cooling the matrix below its $T_g$ in the presence of a poling field. However, this type of chromophore orientation is not in a state of thermodynamic equilibrium. Thus the poled polymer tends to relax to its original random order resulting in the cancellation of the second-order nonlinearity.

For a second-order NLO polymeric material to be useful in most practical applications, it is necessary that the poled polymer is able to maintain a substantial degree of poled order and associated bulk nonlinearity at operating temperatures at least as high as 80 °C for years, as well as at processing temperatures that may exceed 250 °C for short

periods of time.[5] Therefore, such a relaxation of the poled order in the polymer has to be minimized. The stabilization of the poled order has been enhanced in polymeric films by different approaches as reported in a large volume of literature over the past few years.[1] In guest/host systems where NLO chromophores are dissolved in polymer matrices, the matrix needs to possess a high $T_g$ to obtain good stability. This is due to the fact that the relaxation of the poled order is closely related to the $T_g$ of the polymer.[5] Covalent attachment of the NLO chromophores to the main chain or side chain of the polymers has also been reported to enhance the temporal stability of the poled systems.[1,6-9] Another approach is to employ crosslinking reactions to enhance stability of the second-order NLO properties in several poled polymer systems.[10-15] Dense three-dimensional networks have been prepared by thermal,[10-12] photochemical,[13] or sol-gel reactions.[14,15] The resulting crosslinked polymer has a higher $T_g$ and a network structure which restrict the mobility of the polymer chains. From our previous report,[12] although doping of a crosslinkable dye in a typical thermally crosslinked epoxy-based polymer has lowered the $T_g$ of the polymer, an enhancement of the temporal stability as a direct result of the increased crosslinking density was observed. Thus polymers with high $T_g$ as well as high degree of crosslinking density are sought to improve the temporal stability of the second-order NLO properties. However, slow decay of second-order optical nonlinearity at elevated temperatures was still observed in the polymers.

An interpenetrating polymer network (IPN) is a structure in which two or more networks are physically combined.[16-18] The intimate combination of different networks in the IPN is carried out in a manner such that there are no induced crosslinks between individual polymers. Some permanent entanglements between the different crosslinked networks are certain to occur in any IPN. These permanent entanglements act like the covalently bound chemical crosslinks. The chain entanglements restrict the motion of polymer segments allowing the IPN to be able to significantly suppress the creep and flow phenomena observed in polymers.[17,18] This attractive ability of the IPN provided the motivation for the creation of an IPN as a second-order NLO polymer. The extensively crosslinked networks and the permanent entanglements which are intrinsic characteristics of IPNs have shown potential for restricting the mobility of the aligned

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NLO chromophores, which should greatly enhance the stability of the NLO properties. A high $T_g$ is also essential for a material to exhibit excellent long term stability of second-order NLO properties at elevated temperatures. By appropriate choice of materials that would lead to the formation of two rigid networks, an IPN can also possess an extremely high $T_g$.

When an IPN is prepared for optical applications, light scattering due to phase separation in the sample is a major concern. Materials for optical applications must possess superior optical quality (transparency, uniformity, free from defects that scatter light). Thus to achieve low scattering loss, phase separation in the IPN has to be minimized or prevented. Phase separation can be minimized thermodynamically by choosing miscible polymers. Selection of a pair of polymers containing similar functionalities or containing functional groups that can promote intermolecular interactions, e.g. hydrogen or ionic bonding, will increase the development of phase mixing. Homogeneity in the IPN can also be promoted by controlling the crosslinking reaction of each network to proceed simultaneously.[18] This simultaneous synthesis route is the method of choice for the preparation of NLO-active IPNs as it also facilitates the poling process. This method allows the poling process to be carried out simultaneously with the network formation. The mobility of the monomers, prepolymers, or linear polymers at elevated temperatures is large enough to allow the NLO chromophores to align effectively along the direction of the electric field before the crosslinking reaction can take place. Once both networks are fully formed, the orientation of the poled NLO chromophores are expected to be firmly preserved by the newly formed networks.

An NLO-active semi-IPN has been prepared earlier by physically combining a high $T_g$ polyimide and a sol-gel based polymer network with a high degree of crosslinking. The network is formed by a sol-gel process[19] which involves a sequential hydrolysis and polycondensation of an alkoxysilane (Scheme 1). During the formation of the semi-IPN, the internal production of water due to the imidization of polyamic acid aids the hydrolysis of the sol-gel process. Transparent semi-IPN films containing NLO moieties were obtained after simultaneous thermal curing and poling for 4 h at 220 °C. The $\alpha$ transition of the semi-IPN (E" peak temperature at 298 °C) was found to occur at a

higher temperature than that of the undoped polyimide (E" peak temperature at 288 °C) in dynamic mechanical and dielectric analyses.[20] The poled semi-IPN sample shows excellent temporal stability at room temperature. The poled semi-IPN sample shows a stable second-order NLO property after a small initial decay of 27% from its initial value, as it is subjected to a thermal treatment at 120 °C for over 168 h.

<div align="center">Insert Scheme 1</div>

In this paper, we discuss our approach to achieve stable second-order NLO polymers by adopting the concept of full-IPN. Scheme 2 shows a schematic diagram for the formation of an NLO-active IPN. The NLO-active IPNs are formed by combining two rigid NLO-active crosslinked polymers.[21,22] One of the components is an NLO-active thermally crosslinkable epoxy-based polymer, where the network is formed via a free radical addition polymerization. The other component is a phenoxysilicon polymer where the network is formed through a sol-gel reaction. Upon heating to high temperatures, these two polymer networks would form noninterferingly and simultaneously. Mobility of the NLO chromophores in the IPNs is restricted because the polymers are interlocked by the entanglements of the extensive three dimensional network.

<div align="center">Insert Scheme 2</div>

## II. Experimental

### a. IPN-A

This IPN sample is established by combining two rigid NLO-active polymer networks.[21] One component is an epoxy-based polymer functionalized with acryloyl groups (BPAZO), the other is a phenoxysilicon polymer based on a multifunctional phenoxyl compound (THPE), and an alkoxysilane dye (ASD). Scheme 3 shows the chemical structures of BPAZO, THPE, and ASD. BPAZO forms a network through acryloyl groups which are reactive at high temperatures without the aid of any catalyst or initiator. The phenoxysilicon polymer network is formed by the sol-gel process in a

base-catalyzed condition. Both polymers are well characterized and their properties have been reported in refs 12 and 15, respectively.

Insert Scheme 3

Samples used for the studies were prepared in the form of thin films which were solution-cast on glass substrates by means of a spin-coating technique. ASD and THPE with molar ratio of 1.0 : 1.17 were first dissolved in a mixed solvent (propylene glycol methyl ether acetate : 1,4-dioxane = 3 : 1(v/v)) with a small amount of water and base catalyst. BPAZO, which was dissolved in the same solvent was subsequently added to this solution. The resulting solution contains a weight ratio of 1 to 1 for BPAZO to ASD/THPE. The solution was then spin-coated onto glass microscope slides to form optical quality thin films. The networks of BPAZO and ASD/THPE were formed simultaneously when the thin film was heated at 200 °C on a hot stage. The curing time was chosen to be 60 min to allow for sufficient crosslinking. The typical thickness of the cured films was approximately 0.6 μm.

b. IPN-B

The IPN-B system consists of the network of the phenoxysilicon polymer similar to that used in the IPN-A sample, and a network of a second NLO-active epoxy-based polymer (BPDOMA, Scheme 4) and a thermally-crosslinkable NLO chromophore (DRMA, Scheme 4).

Thin films were prepared in the same manner as for the IPN-A samples. IPN-B samples contained 2:1 weight ratio of the phenoxysilicon to BPDOMA/DRMA, where the weight ratio of BPDOMA to DRMA was 2:1. The network of each prepolymer was formed simultaneously when the thin films were heated for 1 h at 200 °C on a hot stage. The typical thickness of the cured IPN-B films was approximately 1 μm.

Insert Scheme 4

## III. Results and Discussions

### a. IPN-A

The compatibility of these two polymers arises from interactions between the individual polymers. Organic polymers that contain functional groups such as carbonyls or ether oxygens can exhibit hydrogen bonding interactions with the silicon oxide networks.[23] Thus, the BPAZO polymer is capable of forming hydrogen bonds with the phenoxysilicon polymer. In addition, the similarity of the NLO chromophores incorporated in both networks also assists the compatibility of the two networks. During the poling/curing process, the corona field was applied as the temperature was raised to 80 °C. The temperature was then slowly increased to 200 °C and maintained at this temperature for 1 h with the corona field on. The formation of the networks and the molecular alignment for the poled order proceeded simultaneously during this period. The sample was then cooled down slowly to room temperature before the corona field was switched off. It is also noteworthy to mention that the NLO chromophores should be sufficiently aligned during the poling/curing process before the crosslinking reactions of both networks have fully taken place. It is desirable that $T_g$s of the uncured prepolymers are lower than the curing temperature. A high processing temperature in this case provides higher degree of crosslinking reactions. The IPN shows excellent optical quality before and after simultaneous poling and curing.

The homogeneity of this IPN-A system is also suggested by the single $T_g$ at 176 °C observed from the DSC thermogram with a 10 °C/min scanning rate. The $T_g$ of the cured phenoxysilicon and BPAZO samples were determined to be 110 and 178 °C, respectively.

Optical microscopy reveals a clear transparent featureless film. The optical loss measurement on a slab waveguide made from this IPN-A showed a value of 8 dB/cm at 1.3 $\mu$m.[24] The high loss might be attributed to the absorption of the NLO chromophores and the polymers as well as the scattering sites formed during sample preparation.

The temporal stability of second-order nonlinearity of the poled/cured IPN, BPAZO, and phenoxysilicon samples are shown in Figure 1. The IPN system shows no measurable decay of second-harmonic (SH) intensity after being heated at 110 °C for

1000 h, whereas the BPAZO and the phenoxysilicon samples show fast initial reduction of the SH intensity upon heating at 100 and 105 °C, respectively. The NLO coefficients, $d_{33}$, of the poled IPN sample are determined to be 33 pm/V and 5.5 pm/V at 1.064 and 1.542 $\mu$m respectively. The $d_{33}$ values of the poled/cured BPAZO and phenoxysilicon samples have been reported earlier to be 18 and 77 pm/V at 1.064 $\mu$m, respectively.[12,15] In addition to the stability created by the high $T_g$ of the polymers and high crosslinked density, this synergistic stability of SH intensity for the IPN system is a result of the permanent entanglements between the two networks which further constrain the motion of aligned chromophores. Therefore, the mobility of the NLO chromophores is significantly decreased which enhanced the temporal stability of the poled order. This confirms the important role of permanent entanglements between the two networks on the stability enhancement.

Insert Figure 1

The nature of the relaxation process of the poled order in the IPN-A system[25] is found to be fundamentally different from that of typical guest/host and side-chain systems.[5,26] The decay of the second-order nonlinearity as a function of time in this IPN was investigated in the range from 110 to 170 °C. The stability of this IPN is superior to those of classic guest/host polymers as indicated by longer relaxation times at temperatures from 110 to 130 °C. The relaxation process of the IPN system follows Arrhenius type behavior at temperatures ranging from 140 to 170 °C. A direct comparison between the relaxation behavior of the guest/host systems and that of the IPN system leads to the conclusion that the IPN systems not only provide better long term stability but also exhibit much better stability than that of the guest/host and side-chain systems at temperatures near the $T_g$ of the polymers.

b. IPN-B

This IPN is prepared with a slight modification of the chemical structure of the epoxy-based polymer used in the IPN-A, in order to improve the optical transparency of the sample. Moreover, a thermally crosslinkable NLO chromophore is added as a guest molecule in order to increase the chromophore density as well as crosslinking density of the sample.[22]

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BPAZO is different from BPDOMA only that the former is functionalized (around 30 %) with acryloyl groups while the latter is highly functionalized (closed to 100 %) with methacryloyl groups. DRMA contains two methacryloyl groups which are thermally crosslinkable. This thermally crosslinkable chromophore will help increase the crosslinking density in the epoxy-based network. The alignment of the NLO chromophores and the formation of both networks are achieved simultaneously upon heating at 200 °C for 1 h. The transparent IPN-B film shows a single $T_g$ at 141 °C from a DSC scan at 10 °C/min. The $T_g$ of the cured phenoxysilicon polymer and BPDOMA are determined to be 110 and 145 °C, respectively. The poled IPN-B film exhibits a $d_{33}$ of 26 pm/V at 1.064 $\mu$m. The poled/cured BPDOMA and BPDOMA/DRMA (1:1 wt ratio) samples exhibit $d_{33}$ of 34 and 28 pm/V at 1.064 $\mu$m, respectively. Temporal stability of the second-order nonlinearity of the IPN-B compared to that of its parent polymers is shown in Figure 2. The temporal stability of the optical nonlinearity of the IPN-B is synergistically enhanced in a similar fashion to the case of the IPN-A. The superiority of the temporal stability of the IPN-A over that of the IPN-B is on account of the higher $T_g$ of the former.

Insert Figure 2

Optical loss of the IPN-B samples was determined to be 4 dB/cm at 1.3 $\mu$m.[27] The lower optical loss in the IPN-B has demonstrated that a slight modification of the chemical structures from BPAZO to BPDOMA has resulted in an improvement in the optical quality of the materials. The large degree of functionalization of methacryloyl groups in the case of BPDOMA has significantly reduced the concentration of hydroxyl groups in the polymer. This perhaps has played an important role in the reduction of the absorption loss[28] and resulted in the improvement of the optical quality of the IPN-B. The results from the optical loss measurements also confirm that phase separation did not occur in these IPN samples. However, some scattering sites which could probably result from some micro voids when water and alcohol were released during the formation of the networks might be responsible for the optical loss in the IPN samples.

## IV. Conclusions

The stability of the IPN samples demonstrated here has shown that the IPN is a promising approach to obtain stable second-order NLO materials. Synergistic enhancement of the temporal stability has been observed in the IPN samples. The diversity of the molecular design for the IPN has opened a door for materials with better properties to be developed. For example, in order to modify the IPN-A or IPN-B, THPE molecule may be replaced by a phenolic compound which is part of an NLO chromophore. A variety of choices of crosslinked networks can be prepared to possess high $T_g$s. Chromophores with large NLO responses can also be incorporated into the IPNs to boost up the optical nonlinearity of the materials. Properties of the IPN can be fine-tuned by altering the chemical structures, composition, or processing conditions for the development of materials with optimized properties.

## V. Acknowledgments

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## Figure Captions

Scheme 1.    Typical reaction mechanism of a sol-gel process. Network formation is achieved through water and alcohol condensation.

Scheme 2.    Schematic for the formation of an NLO-active IPN film. Noncentrosymmetric alignment of NLO chromophores can be obtained by simultaneous poling and curing the spin-coated film.

Scheme 3.    Chemical structures of (a) BPAZO, (b) ASD, and (c) THPE.

Scheme 4.    Chemical structures of (a) BPDOMA and (b) DRMA. Both compounds were functionalized with the same thermal crosslinkable methacryloyl group.

Figure 1.    Temporal behavior of the effective second-harmonic coefficient of the poled IPN-A, the poled/cured BPAZO, and phenoxysilicon samples at elevated temperatures.

Figure 2.    Temporal behavior of the effective second-harmonic coefficient of the poled IPN-B, the poled/cured BPDOMA/DRMA and phenoxysilicon samples treated at 100 °C for over 168 h.
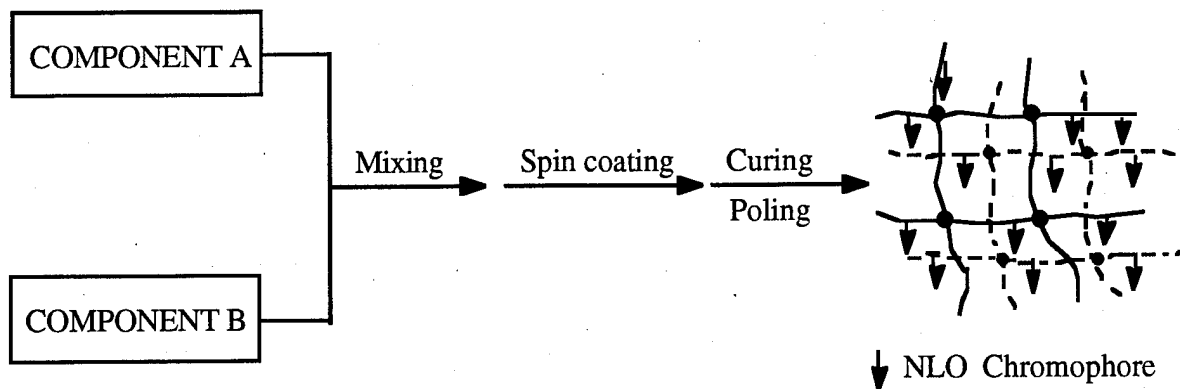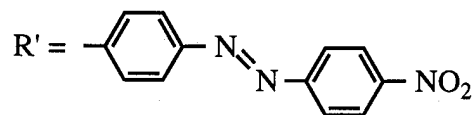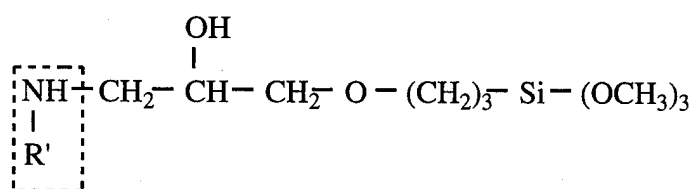
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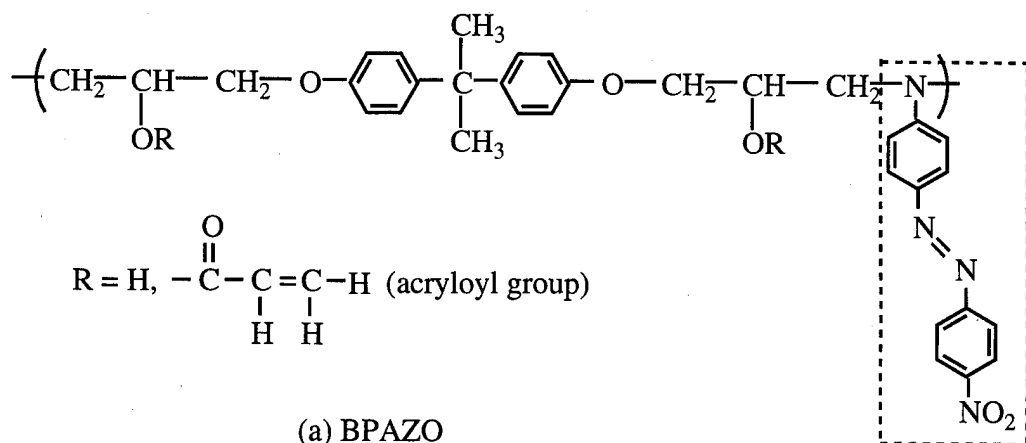
$$\equiv Si-OR + H_2O \quad \rightleftharpoons \quad \equiv Si-OH + R-OH$$

water condensation

$$\equiv Si-OH + HO-Si\equiv \quad \rightleftharpoons \quad \equiv Si-O-Si\equiv + H_2O$$

alcohol condensation

$$\equiv Si-OH + RO-Si\equiv \quad \rightleftharpoons \quad \equiv Si-O-Si\equiv + R-OH$$

COMPONENT A

COMPONENT B

Mixing    Spin coating    Curing
                          Poling

↓ NLO  Chromophore

(a) BPAZO

R = H, −C(=O)−CH=CH−H (acryloyl group)

(b) ASD

$R' = $ −C$_6$H$_4$−N=N−C$_6$H$_4$−NO$_2$

(c) THPE

= NLO-active moiety

$\left(CH_2{-}CH{-}CH_2{-}O{-}\right.$ [benzene ring] $\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}$ [benzene ring] $O{-}CH_2{-}CH{-}CH_2{-}N{-}\left.\right)$

with $OR$ below the $CH$ groups

$R = -\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=\overset{\overset{H}{|}}{C}-H$ (methacryloyl group)

(a) BPDOMA

NLO-active moiety: —N— [benzene ring] —N=N— [benzene ring] —NO$_2$
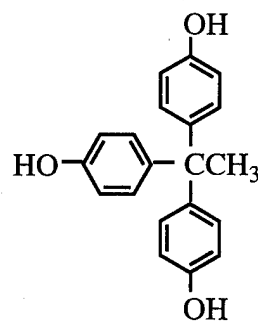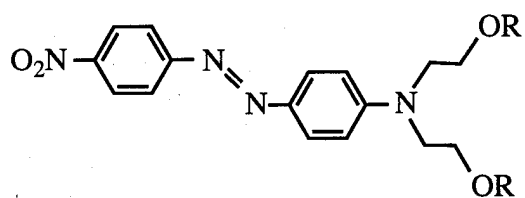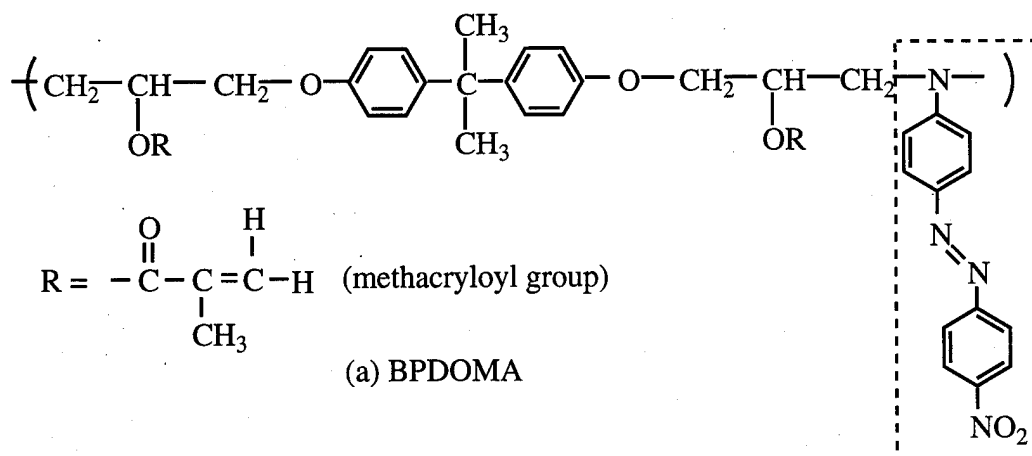
(b) DRMA (NLO-active chromophore)

$O_2N-$ [benzene ring] $-N=N-$ [benzene ring] $-N\begin{cases} OR \\ OR \end{cases}$

$\boxed{\phantom{xxxx}}$ = NLO-active moiety